Ab initio thermodynamics for the design of energy materials

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Computational materials modelling allows researchers to examine novel, rare, dangerous or even impossible compounds to gain insight while avoiding traditional practical limits. Such methods are especially suitable for energy materials, which tend to be highly-pure semiconductors doped with rare elements. Increasing computational power and sophistication has driven a steady increase in scale and accuracy, and recently it has become feasible to study chemical reactions in more detail by linking *ab initio* methods to classical thermodynamics.

Chemical thermodynamics

Materials modelling typically focuses on enthalpy, H, a measure of the heat associated with a reaction. The vast majority of this energy is due to electronic structure; temperature and pressure play a role but these are often neglected in the solid state.

$$H = E_{\text{Electronic}} + E_{\text{Vibrational}} + PV$$

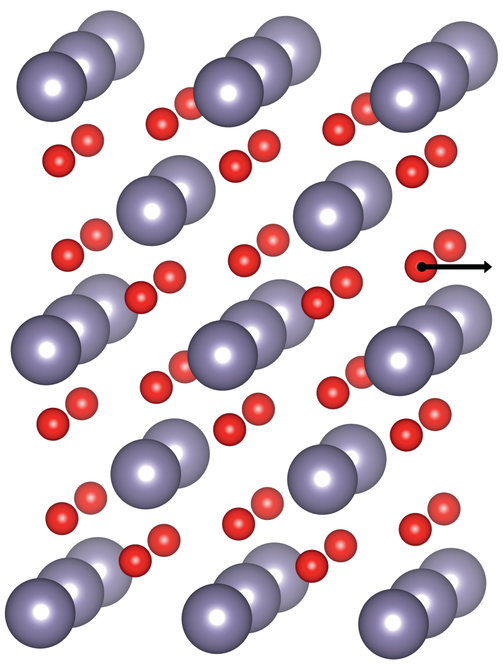
$$H = E_{\text{DFT}} + E_{\text{zero-point}} + \int_0^T C_p \mathrm{d}T + PV$$

where E_{DFT} is the ground-state energy of the electronic structure, calculated with density functional theory (DFT). Enthalpy changes are easy to relate to experimental results, even when the temperature, pressure and zero-point energy terms are neglected. However, for the study of chemical reactions it is more important to consider the Gibbs free energy, which incorporates entropy. A negative change in Gibbs free energy is associated with a spontaneous reaction.

$$G = H - TS$$

$$G = E_{\text{DFT}} + E_{\text{zero-point}} + \int_0^T C_p \mathrm{d}T + PV - TS$$

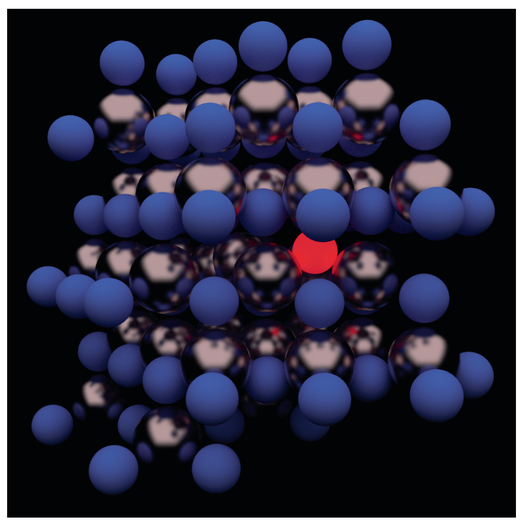
Phonon calculations



Entropy and heat capacity are largely derived from lattice vibrations. In order to obtain vibrational energies from first principles, a set of independent vibration "modes" is found. In the "direct method", energy changes are calculated for a series of small displacements of individual atoms using DFT (or other theoretical methods). The atoms are assumed to be small harmonic oscillators, yielding a set of energies which are filled according to classical thermodynamics.

The general goal in materials modelling is to improve methods to the point that they readily achieve "chemical accuracy". As well as taking advantage of developments in quantum chemical methods, computer hardware and algorithms, a sound thermodynamic framework is needed to bring these models to real-world reaction conditions.

Case study: Oxidation of GaN



Oxygen defect in GaN

GaN is a key material in high-efficiency LED lighting, with potential applications in photovoltaics and high-power switching. In an *ab initio* study, the equilibrium formation of oxygen defects was examined. These defects have a significant effect on the electronic structure of the material. It was confirmed that the solid-gas equilibrium is sensitive to temperature and pressure, but favours oxidation in practical conditions.

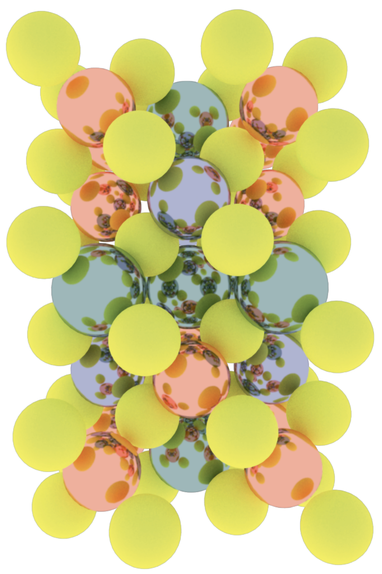
Computational details

In the projects discussed here, the FHI-aims quantum chemistry code is used for DFT calculations. Calculations are carried out on a range of systems: Neon is a group-owned cluster accommodated by the University HPC facility alongside Aquila. HECToR is the national supercomputer, accessed via our membership of the UK Materials Chemistry Consortium, and we have been testing Blue Joule via an STFC early-access program. FHI-aims is especially suited to large systems and scales well on massively-parallel architectures. Data processing on local workstations uses custom MATLAB and Python code, as well as the Phonopy project.

	Crystal structures (1-100 atoms)	Phonon calculations (100 x 100 atoms)
	Simple gases	Expanded supercells, surfaces, defects (>50 atoms)
	Detailed electronic structure for small systems	
	Results processing plotting, imaging	

	Workstation	**Neon**	**Aquila**	**HECToR**	**Blue Joule**
Typical job size (cores)	4	24	64-128	512-2048	1024-8192
Typical walltime	Unlimited	Unlimited	Days	12 hr	1 hr

Case study: formation of CZTS



Cu_2ZnSnS_4 (CZTS) is a promising material for Terawatt-scale photovoltaics, being composed of abundant elements and an effective absorber in very thin films. An initio thermodynamics is being applied to compare the wide array of synthesis routes and phases involved in this complex system. The goal is an industrial process which is truly scalable, producing high-quality thin film solar cells.

Further reading:

Walsh, A. et al., Computational Approaches to Energy Materials 2013, Wiley

Yip, S. (Ed.) *Handbook of materials modelling* 2005**, A**, pp. 149-234, Springer

Lee, J.G., *Computational Materials Science: An Introduction* 2012, CRC press

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